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# Nucleosynthetic molybdenum isotope anomalies in iron meteorites – new evidence for thermal processing of solar nebula material

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ABSTRACT

We have investigated nucleosynthetic Mo isotope anomalies in 38 different bulk iron meteorites from 11 groups, to produce by far the largest and most precise dataset available to date for such samples. All magmatic iron groups were found to display deficits in s-process Mo isotopes, with essentially constant anomalies within but significant variations between groups. Only meteorites of the non-magmatic IAB/IIICD complex revealed terrestrial Mo isotopic compositions.

The improved analytical precision achieved in this study enables two isotopically distinct suites of iron meteorites to be identified. Of these, the *r=p suite* encompasses the IC, IIAB, IIE, IIIAB, IIIE and IVA groups and exhibits relatively modest but 'pure' s-process deficits, relative to Earth. The second *r>p suite* includes groups IIC, IIIF and IVB. These iron meteorites show larger s-process deficits than the *r=p suite*, coupled with an excess of r-process relative to p-process components.

Comparison of the results with data for other elements (e.g., Cr, Ni, Ru, Ti, Zr) suggests that the Mo isotope variability is most likely produced by thermal processing and selective destruction of unstable presolar phases. An updated model is proposed, which relates the iron meteorite suites to different extents of thermal processing in the solar nebula, as governed by heliocentric distance. In detail, the *r=p suite* of iron meteorite parent bodies is inferred to have formed closer to the Sun, where the extent of thermal processing was similar to that experienced by terrestrial material, so that the meteorites exhibit only small s-process deficits relative to Earth. In contrast, the *r>p suite* formed at greater heliocentric distance, where more subtle thermal processing removed a smaller proportion of r- and p-process host phases, thereby generating larger s-process deficits relative to the terrestrial composition. In addition, the thermal conditions enabled selective destruction of p- versus r-isotope carrier phases, to produce the observed divergence of r- and p-process Mo isotope abundances.



## 1. Introduction

The solar system formed from the collapse of a molecular cloud of interstellar dust and gas featuring isotopically diverse material produced by nuclear reactions in various pre-existing stellar sources. Whilst presolar grains in primitive meteorites show this cloud was isotopically heterogeneous at the grain-size level (Zinner, 2007), it was initially thought planetary bodies evolved from a hot solar nebula that was well-mixed on larger scales. Various more recent studies, however, identified isotopic variations in bulk meteorites for a number of refractory elements, which are interpreted to reflect planetary-scale heterogeneities in presolar matter that place critical constraints on the physical conditions within the solar nebula. The isotopic heterogeneities found for elements including Ba, Ca, Cr, Mo, Nd, Ni, Ru, Ti and Zr thereby stand in contrast to the isotopic homogeneity exhibited by other refractory elements such as Hf and Os (see Dauphas and Schauble, 2016 and Yokoyama and Walker, 2016 for a thorough overview).

Molybdenum is ideally suited as a tracer of planetary-scale isotopic heterogeneity because it has seven isotopes that were produced by distinct nucleosynthetic processes. The s-process contri-

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butions to $^{94}$Mo, $^{95}$Mo, $^{96}$Mo, $^{97}$Mo, $^{98}$Mo and $^{100}$Mo are thought to be from the main s-process in asymptotic giant branch (AGB) stars, while the r-process contributions to the neutron-rich isotopes ($^{95}$Mo, $^{97}$Mo, $^{98}$Mo and $^{100}$Mo) are argued to be produced by the weak r-process and charged particle reactions (CPRs) in Type II supernovae, with contributions from the main r-process (e.g., Qian and Wasserburg, 2007). Traditionally, models of p-process nucleosynthesis were unable to reproduce the measured abundances of $^{92}$Mo and $^{94}$Mo, but more recent studies have rectified this problem. In detail, it was proposed that CPRs in the neutrino-driven winds of Type II and photodisintegration reactions ($\gamma$-process) in Type Ia supernovae can account for the observed $^{92}$Mo and $^{94}$Mo abundances (e.g., Travaglio et al., 2015; Wanajo et al., 2011), though this is contested by other workers (e.g., Fisker et al., 2009).

The existence of planetary-scale nucleosynthetic Mo isotope anomalies was first established by the bulk meteorite analyses of Dauphas et al. (2002). A similar but more recent investigation (Burkhardt et al., 2011) used improved methods to produce a comprehensive Mo isotope dataset for a wider range of meteorite types, with a precision several times better than that reported in earlier studies. The latter study found that all chondrites and iron meteorites (except for the non-magmatic IAB/IIICD group), as well as two pallasites, exhibited clear s-process deficits. In contrast, analyses of Martian meteorites and an angrite revealed terrestrial Mo isotope compositions. The authors were therefore able to conclude that Earth, Mars, and the parent bodies of angrites and non-magmatic IAB/IIICD irons accreted from material with a higher proportion of s-process Mo isotopes than the chondrite, pallasite and other iron meteorite parent bodies.

Given the abundance of available data, any model that is proposed to account for the observed nucleosynthetic Mo isotope anomalies should also be able to explain the isotopic heterogeneity or homogeneity found for other refractory elements. A number of such scenarios have been posited, including inefficient/incomplete mixing in the solar nebula (e.g., Schiller et al., 2015), late injection (e.g., Qin et al., 2011), grain size sorting (Dauphas et al., 2010), thermal processing (e.g., Burkhardt et al., 2012b), and parent body processes (e.g., aqueous alteration – Yokoyama et al., 2011). To further elucidate the validity of these concepts, we have obtained precise Mo isotope data for 11 groups of iron meteorites. With better precision than previous studies, the results provide new constraints on planetary-scale processes in the solar nebula and help resolve the origin of nebula-wide nucleosynthetic isotope anomalies.

## 2. Analytical techniques

Only a brief outline of the methods is presented here, with further details available in the Supplementary Material. Fifty-three specimens from 38 distinct iron meteorites of 11 different groups were obtained from the Natural History Museum, London, and private collectors. Separation of Mo was achieved by a two-stage procedure, which applies anion exchange chromatography with Bio-Rad AG1-X8 resin. Following the chemistry, the purified Mo fractions typically had Ru/Mo and Zr/Mo ratios of lower than $3 \times 10^{-5}$ and $4 \times 10^{-5}$, respectively, corresponding to corrections on Mo isotope ratios of less than 50 ppm for Ru interferences, and of less than 100 ppm for Zr.

Isotope measurements were performed with a Nu Plasma HR MC-ICP-MS, in a two-sequence routine. A simultaneous measurement of $^{92}$Mo, $^{94}$Mo, $^{95}$Mo, $^{96}$Mo, $^{97}$Mo, $^{98}$Mo, $^{100}$Mo and $^{99}$Ru ion beams was performed in the first sequence, while the second sequence, which immediately followed the first, collected the $^{90}$Zr/$^{95}$Mo ratio for Zr interference corrections. Typical sensitivity for Mo was 150–180 V/ppm.

Instrumental mass bias was corrected by internal normalisation to $^{98}$Mo/$^{96}$Mo = 1.453174 ('8/6'), $^{92}$Mo/$^{98}$Mo = 0.607898 ('2/8') and $^{97}$Mo/$^{95}$Mo = 0.602083 ('7/5'), using the exponential law (Lu and Masuda, 1994). All sample data are given relative to the mean of several (typically $n = 4$) bracketing runs of NIST SRM 3134 Mo made up to closely match the Mo concentration of the samples (~200 ppb), and reported in $\varepsilon^i$Mo notation (Equation (1)), where $^{9y}$Mo/$^{9x}$Mo is the normalising ratio:

$$\varepsilon^i\mathrm{Mo}_{(y/x)} = \left[ ({}^i\mathrm{Mo}/{}^{9x}\mathrm{Mo})_{\mathrm{sample}} / ({}^i\mathrm{Mo}/{}^{9x}\mathrm{Mo})_{\mathrm{standard}} - 1 \right] \times 10^4 \quad (1)$$

Typical external reproducibility ($2\sigma$ = 2sd) of the standard measurements over a single session ($n > 50$) ranged from ±0.47 for $\varepsilon^{92}\mathrm{Mo}_{(8/6)}$ to ±0.15 for $\varepsilon^{96}\mathrm{Mo}_{(2/8)}$, while internal precision (2se) ranged from ±0.29 to ±0.09 ($\varepsilon^{92}\mathrm{Mo}_{(8/6)}$ and $\varepsilon^{96}\mathrm{Mo}_{(2/8)}$, respectively). The precision achieved here is generally a factor of ~1.5 better than reported in the most precise previous study by Burkhardt et al. (2011). Most likely, the improved precision arises from the higher ion beam intensities that were obtained here for analyses of ~200 ppb Mo solutions, whilst Burkhardt et al. (2011) utilised ~100 ppb Mo solutions.

The robustness and reproducibility of the Mo separation procedure and MC-ICP-MS Mo isotope measurements were repeatedly evaluated by analyses of terrestrial standard reference materials, which yielded the expected Mo isotope compositions throughout (see Supplementary Material).

## 3. Results

All Mo isotope results for normalisation to $^{98}$Mo/$^{96}$Mo and $^{97}$Mo/$^{95}$Mo are summarised in Fig. 1, with corresponding data presented in Table 1 and Table 2. Also shown in Fig. 1 are the expected effects of increasing and decreasing the proportions of p-, s- and r-process components on the Mo isotope patterns. Details of this modelling, as well as the results using normalisation to $^{92}$Mo/$^{98}$Mo, are outlined in the Supplementary Material.

For all normalising schemes, meteorites of all groups (except IAB/IIICD) exhibit offsets from $\varepsilon^i\mathrm{Mo} = 0$. The results agree most with the corresponding models of s-process deficits (solid green lines, Fig. 1c–d). For instance, in the data normalised to $^{98}$Mo/$^{96}$Mo (Fig. 1a), the magnitude of anomalies decreases in the order $\varepsilon^{92}\mathrm{Mo}_{(8/6)} > \varepsilon^{94}\mathrm{Mo}_{(8/6)} > \varepsilon^{95}\mathrm{Mo}_{(8/6)} > \varepsilon^{100}\mathrm{Mo}_{(8/6)} > \varepsilon^{97}\mathrm{Mo}_{(8/6)}$, giving rise to the characteristic w-shaped pattern of s-process deficits, as depicted by the solid green line in Fig. 1c.

Meteorites from the same group display identical or nearly identical Mo isotopic anomalies (within uncertainty), such that the Mo isotope composition of any meteorite can be considered as representative of the complete metal core of its parent body. Yet, the extent of the anomalies displayed by the different magmatic iron groups is variable. The IIC irons display by far the most extreme isotope compositions with $\varepsilon^{92}\mathrm{Mo}_{(8/6)} = +3.12 \pm 0.27$, while the IVAs are the least anomalous of the magmatic iron groups ($\varepsilon^{92}\mathrm{Mo}_{(8/6)} = +0.95 \pm 0.19$). The non-magmatic IAB and IIICD groups, often termed the IAB/IIICD complex (e.g., Wasson and Kallemeyn, 2002), present Mo isotope compositions indistinguishable from terrestrial Mo, while the non-magmatic IIE group is slightly anomalous with $\varepsilon^{92}\mathrm{Mo}_{(8/6)} = +0.86 \pm 0.32$.

## 4. Discussion

### 4.1. Comparison to literature

While the results presented here are more abundant and precise than the data of Burkhardt et al. (2011) for irons, excellent agreement is observed between these two investigations. Principally, Burkhardt et al. (2011) also found that iron meteorite